Syntheses and Properties of Two-Dimensional, Dicationic Nonlinear Optical Chromophores Based on Pyrazinyl Cores

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Supporting Information

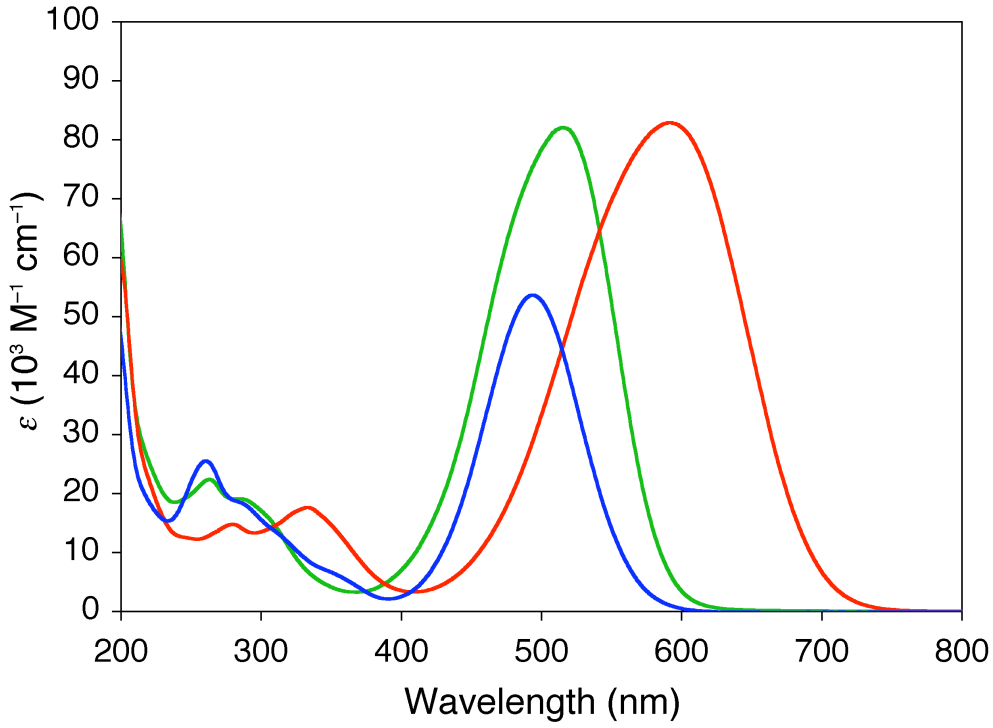

Figure S1. Electronic absorption spectra of the –NMe_2-substituted series [**1**][PF_6]$_2$ (blue), [**2**][PF_6]$_2$ (green) and [**3**][PF_6]$_2$ (red) in acetonitrile at 293 K.

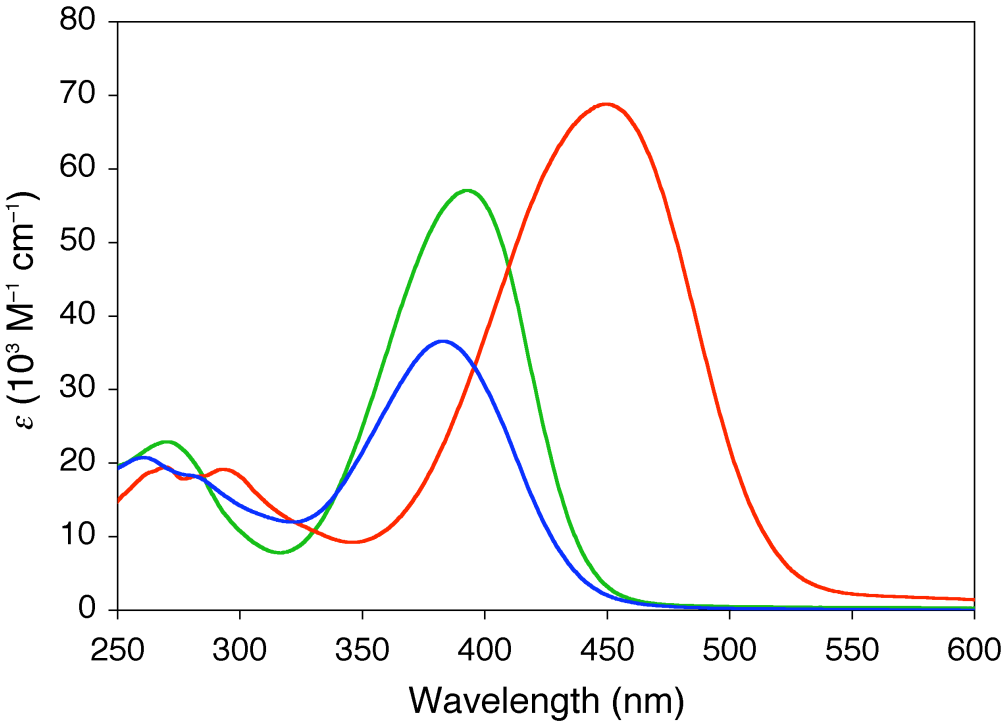

Figure S2. Electronic absorption spectra of the –OMe-substituted series [**4**][PF_6]$_2$ (blue), [**5**][PF_6]$_2$ (green) and [**6**][PF_6]$_2$ (red) in acetonitrile at 293 K.

Original NMR Spectra

Over the following pages NMR spectra (^{1}H in $(CD_3)_2CO$ and ^{13}C in $(CD_3)_2SO$) are presented for all of the new hexafluorophosphate salts described in this paper. Only ^{1}H-NMR spectra are shown for the three nitrate salts (in CD_3OD), which were isolated in smaller quantities primarily for the purpose of obtaining X-ray crystal structures. It should be noted that the relative solubility of the samples is generally moderate to low, and the molecular weights are high, so many of the ^{13}C spectra and some of the ^{1}H spectra show only rather weak signals. All spectra are shown with the full range recorded (0–11 ppm for ^{1}H and 0–200 ppm for ^{13}C), with expansions to show more clearly the aromatic environments. Note that the methyl signals from the $–NMe_2$-based chromophores are obscured by the DMSO solvent signals.

Figure S3. ^{1}H NMR spectrum of [**1**][PF_6]$_2$ (400 MHz in $(CD_3)_2CO$ at 293 K).

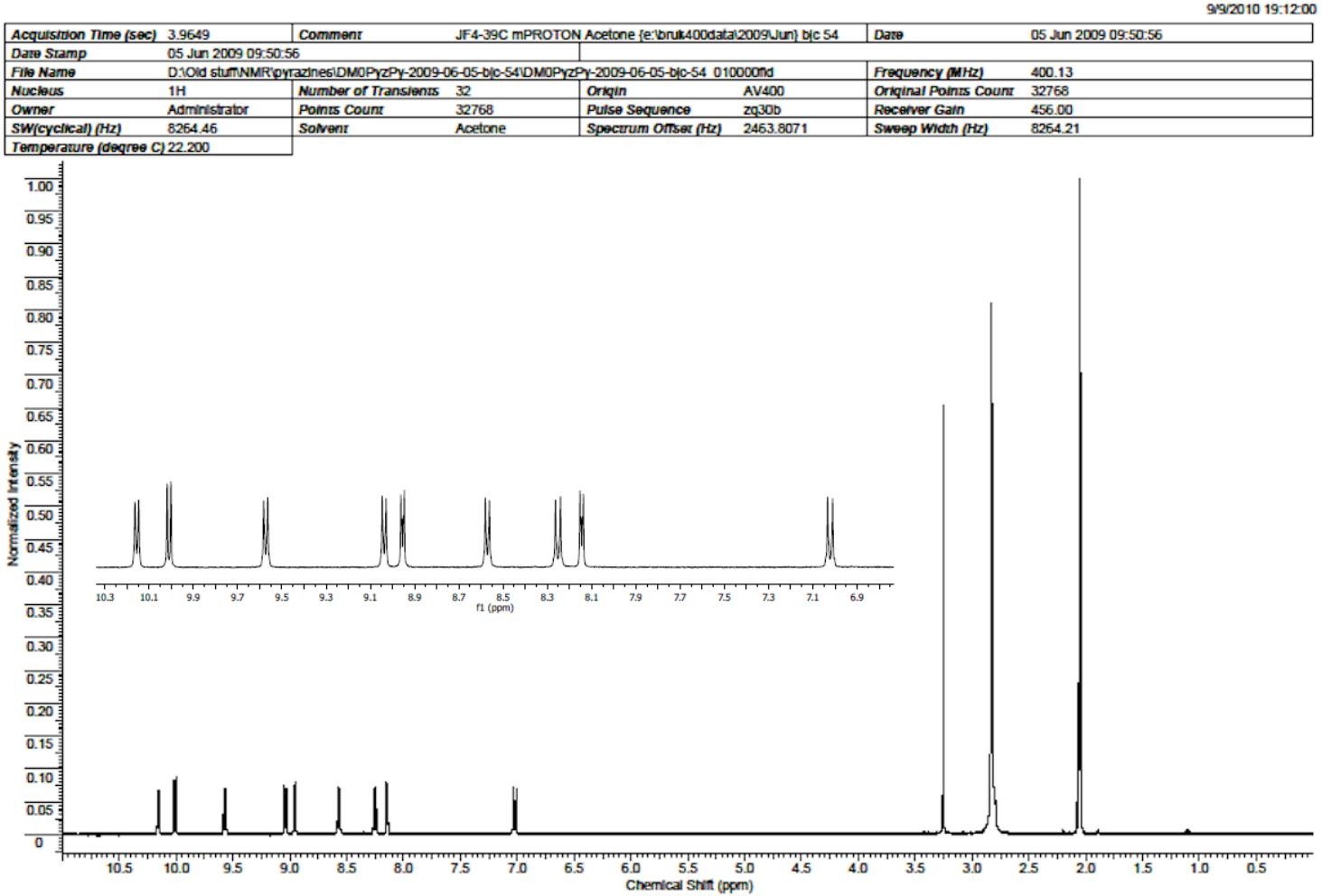

Figure S4. ^{13}C NMR spectrum of [**1**][PF_6]$_2$ (100 MHz in $(CD_3)_2SO$ at 293 K)
(extra expansions show the closely spaced environments at 150.99/150.96 and 145.28/145.25 ppm)

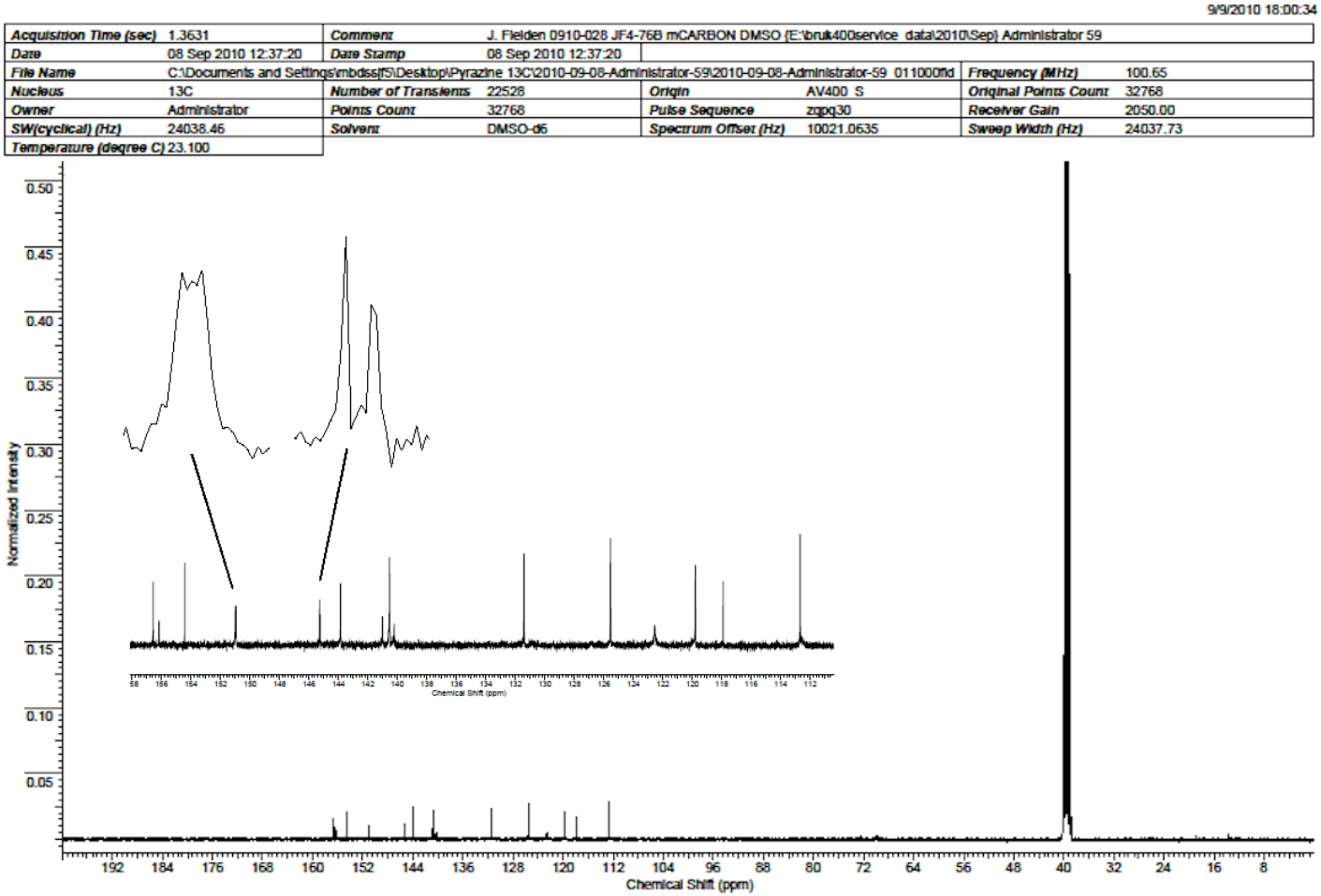

Figure S5. ^{1}H NMR spectrum of [**1**][NO_3]$_2$ (300 MHz in CD_3OD at 293 K).

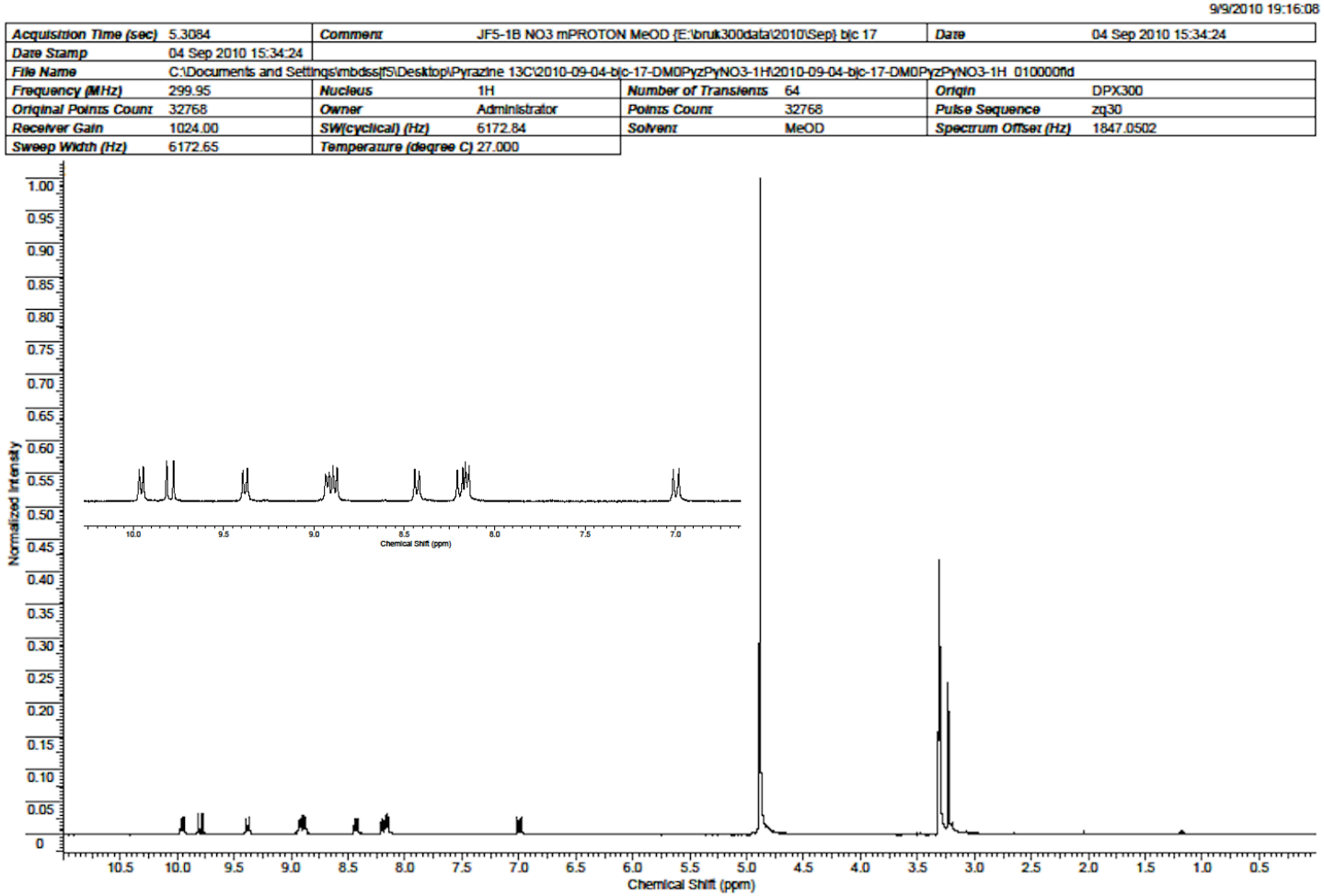

Figure S6. ^{1}H NMR spectrum of [**2**][PF_6]$_2$ (400 MHz in $(CD_3)_2CO$ at 293 K).

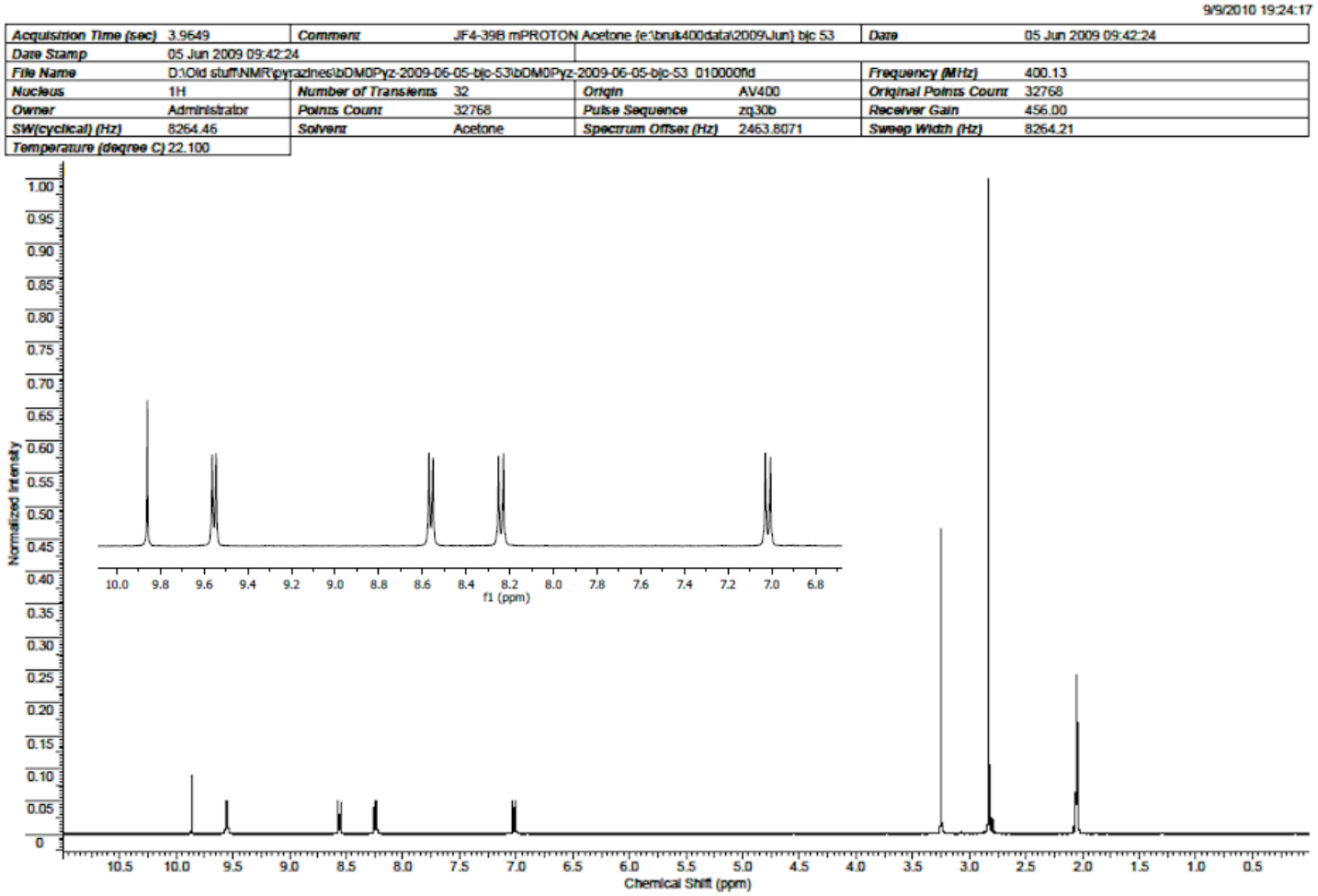

Figure S7. ^{13}C NMR spectrum of [**2**][PF_6]$_2$ (100 MHz in $(CD_3)_2SO$ at 293 K).

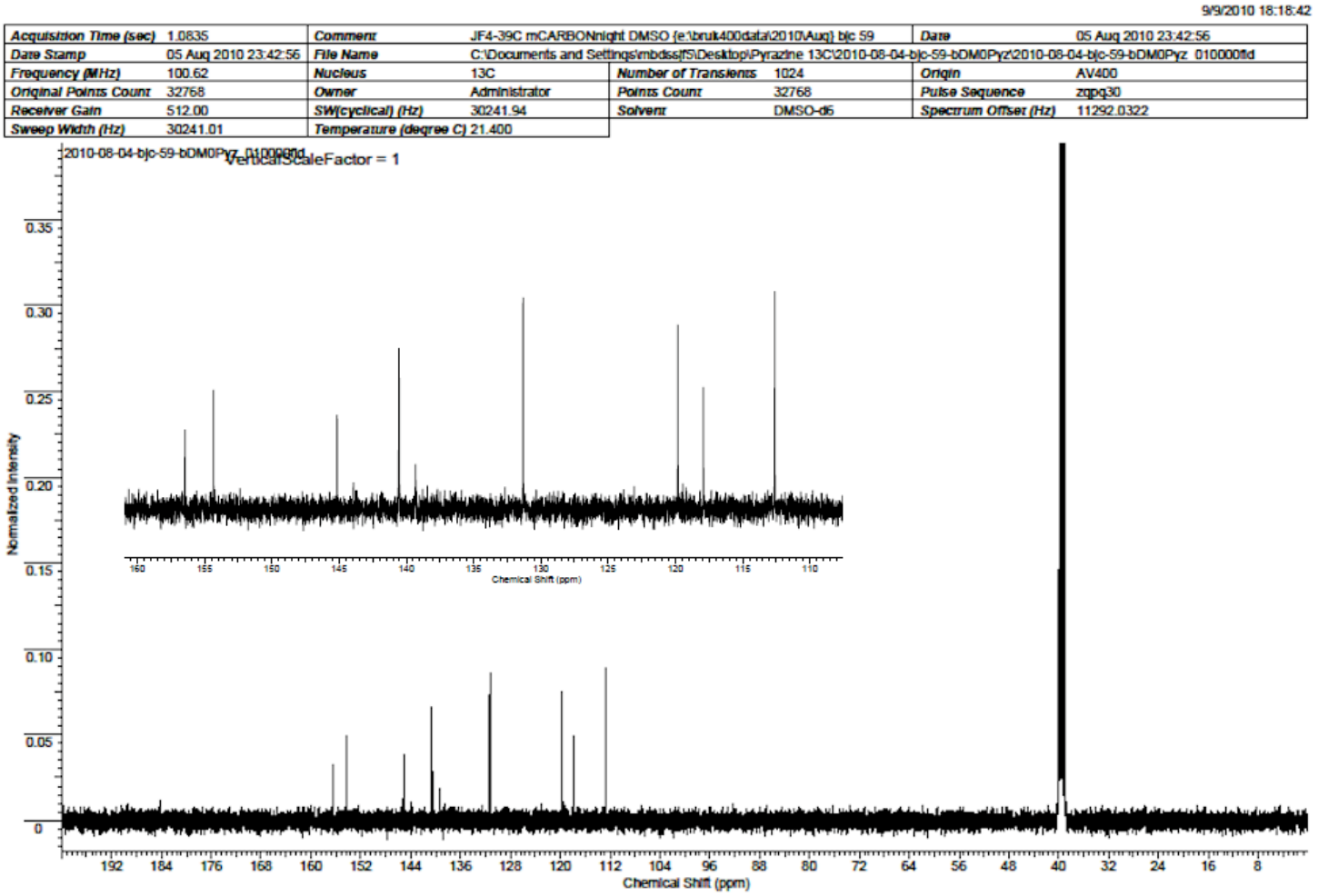

Figure S8. ^{1}H NMR spectrum of [**2**][NO_3]$_2$ (400 MHz in CD_3OD at 293 K).

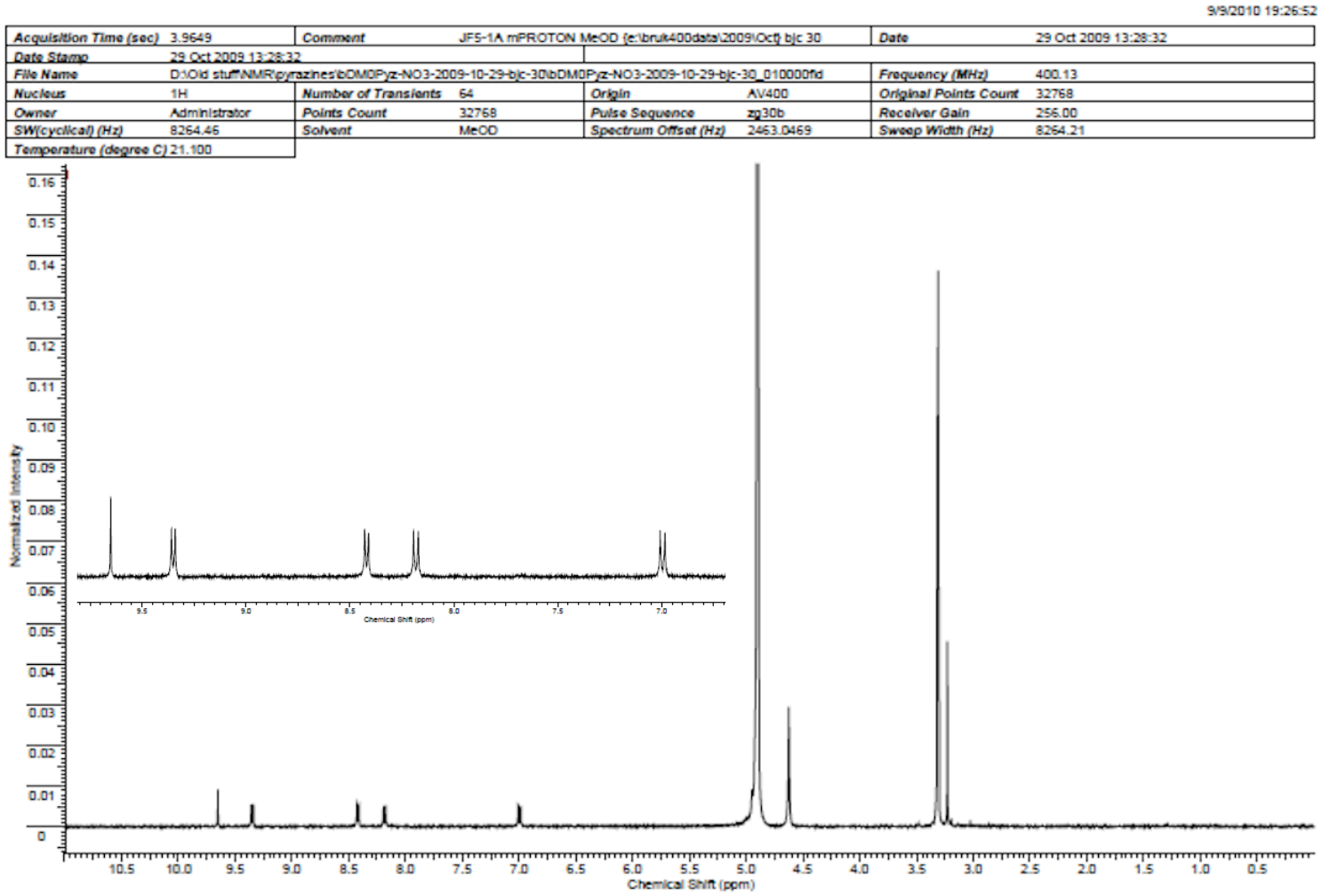

Figure S9. ^{1}H NMR spectrum of [**3**][PF_6]$_2$ (400 MHz in $(CD_3)_2CO$ at 293 K).

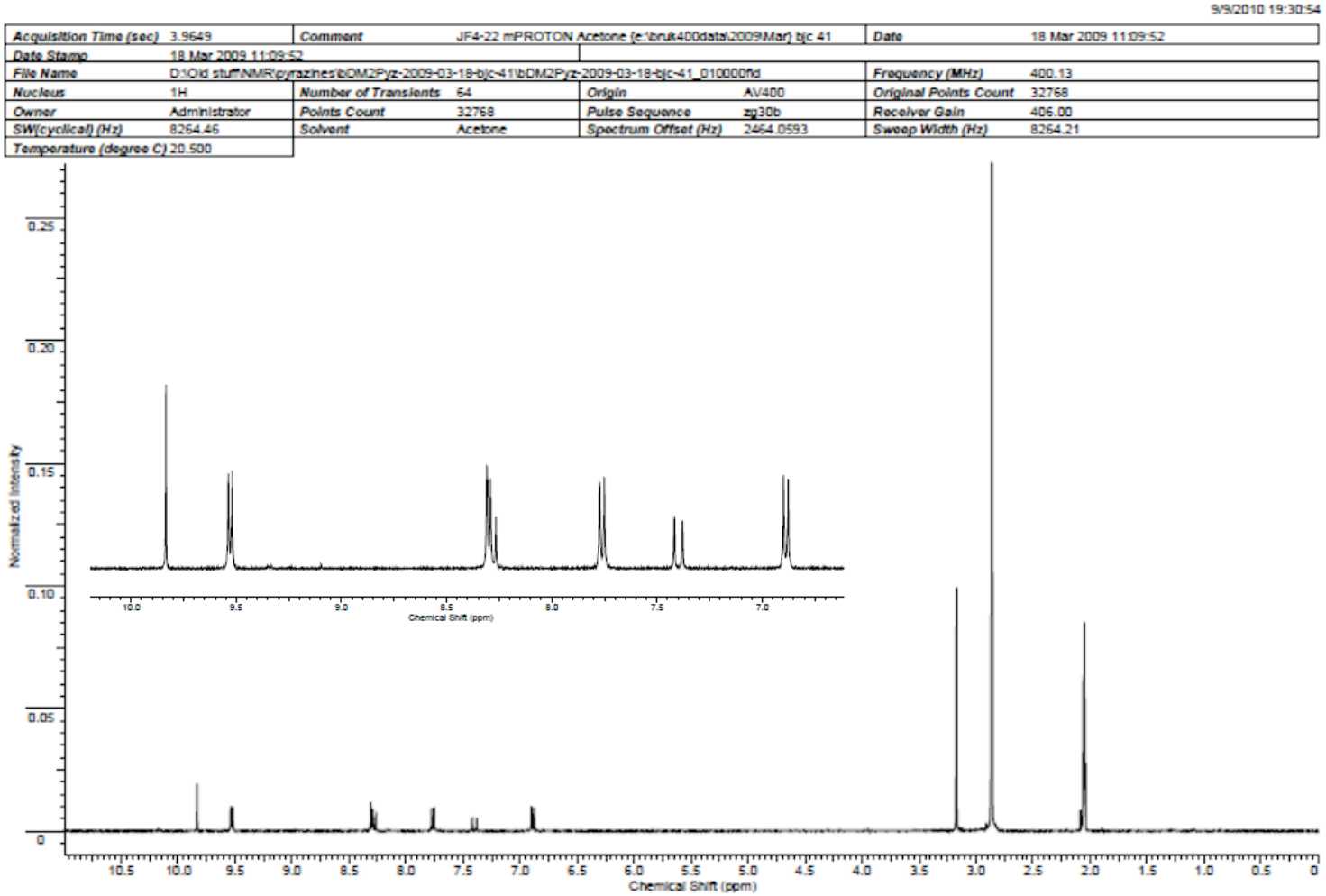

Figure S10. ^{13}C NMR spectrum of [**3**][PF_6]$_2$ (125 MHz in $(CD_3)_2SO$ at 293 K).

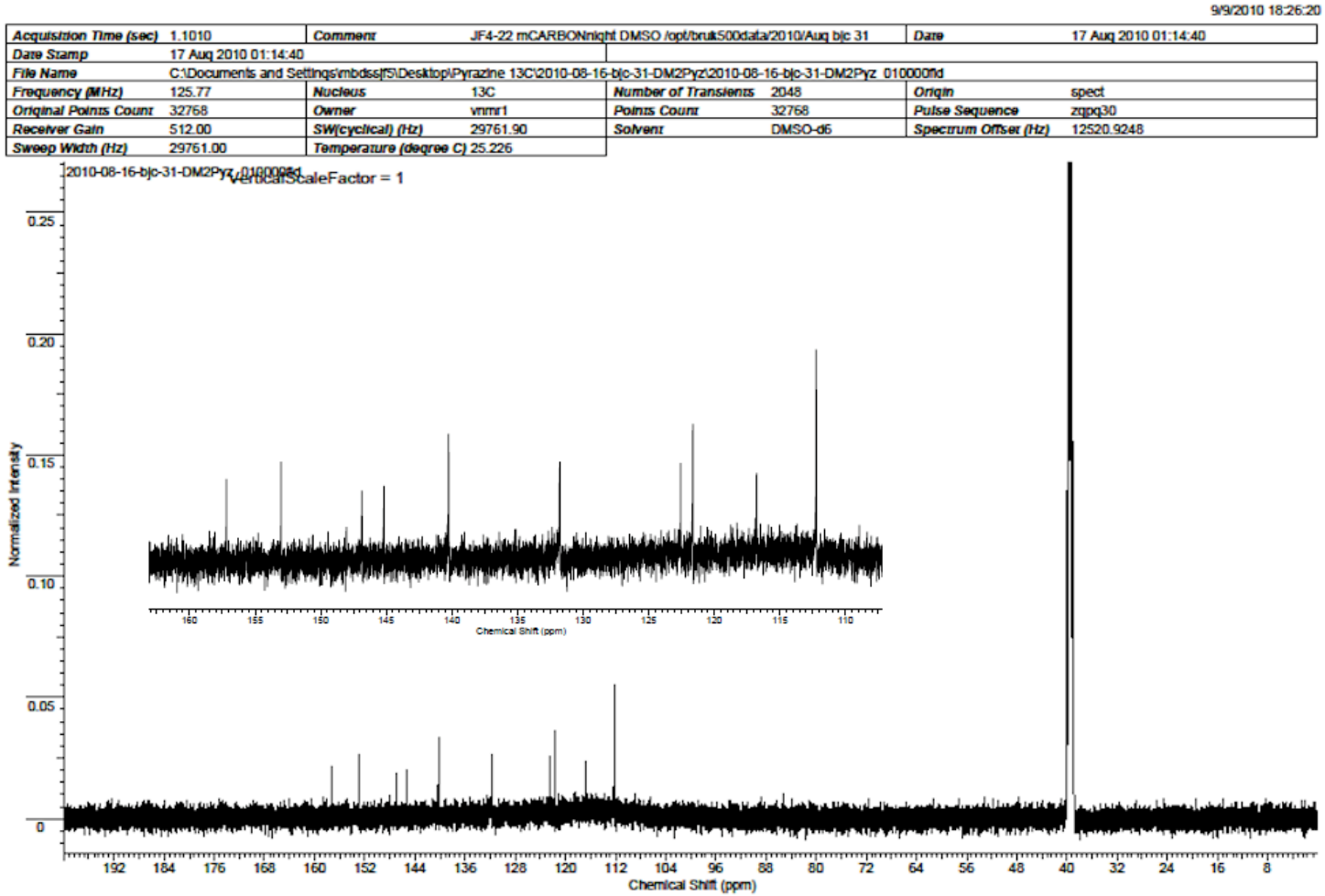

Figure S11. ^{1}H NMR spectrum of [**4**][PF_6]$_2$ (400 MHz in $(CD_3)_2CO$ at 293 K).

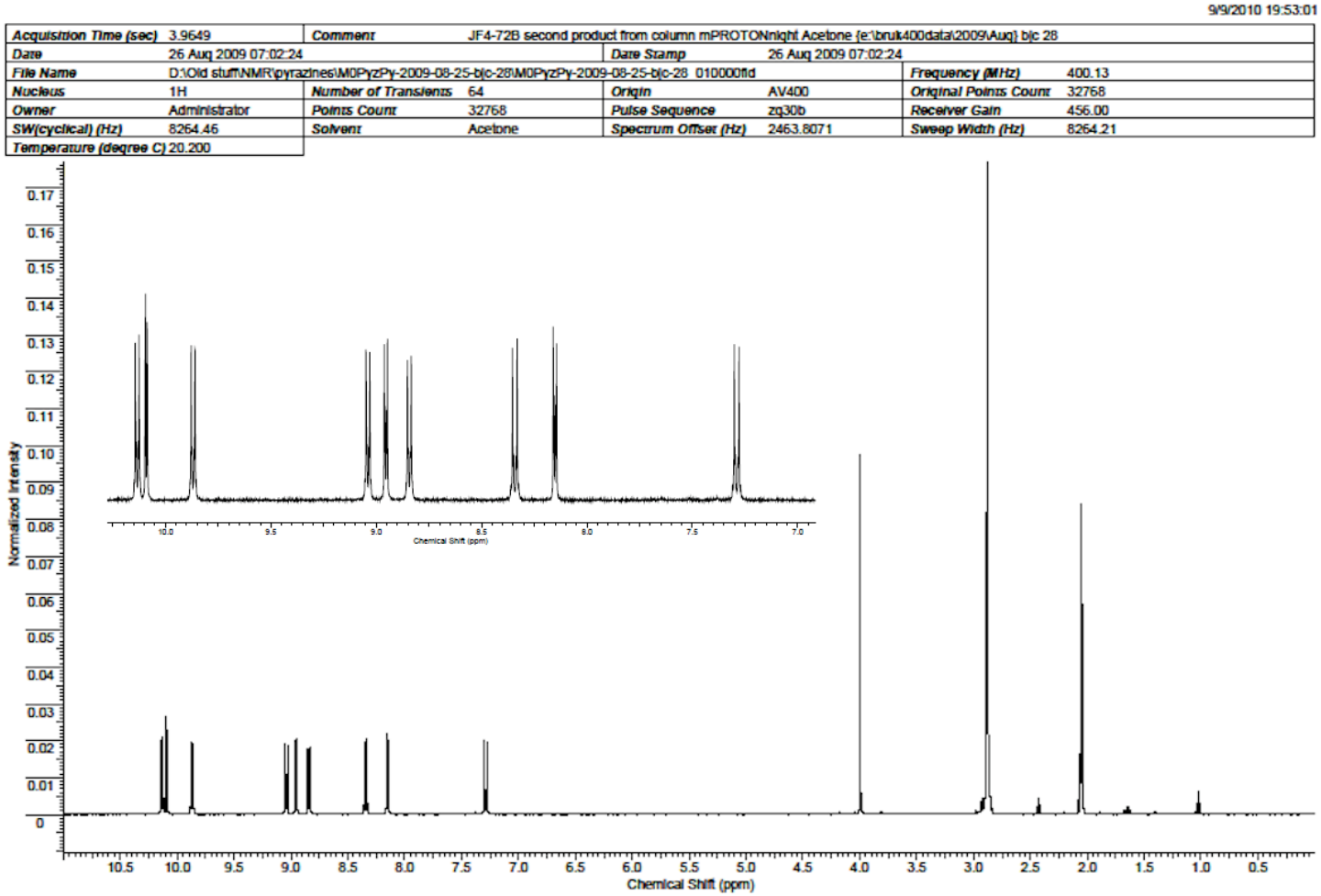

Figure S12. ^{13}C NMR spectrum of [**4**][PF_6]$_2$ (125 MHz in $(CD_3)_2SO$ at 293 K).
(extra expansion shows the closely spaced environments at 145.27/145.25 ppm)

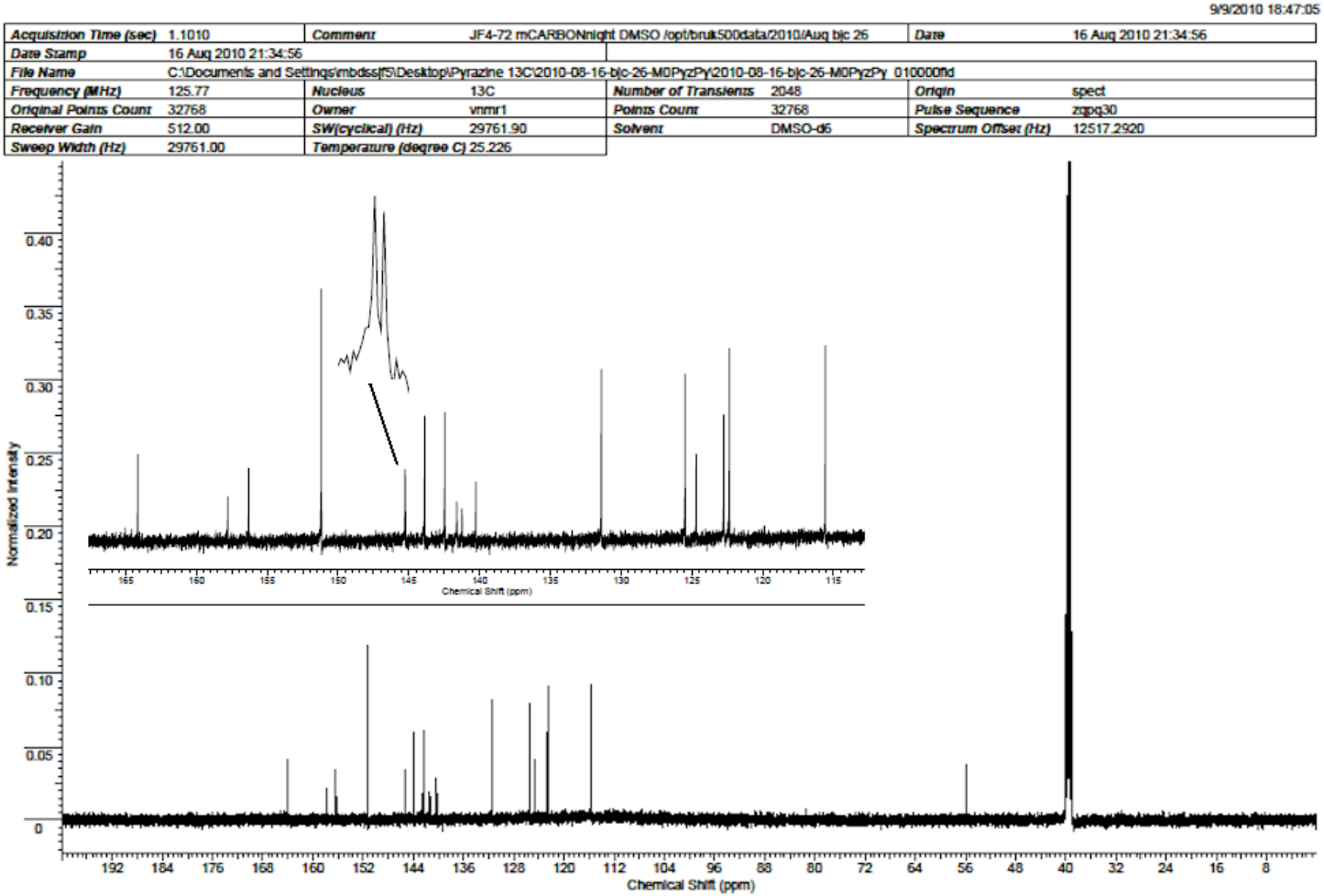

Figure S13. ^{1}H NMR spectrum of [**5**][PF_6]$_2$ (400 MHz in $(CD_3)_2CO$ at 293 K).

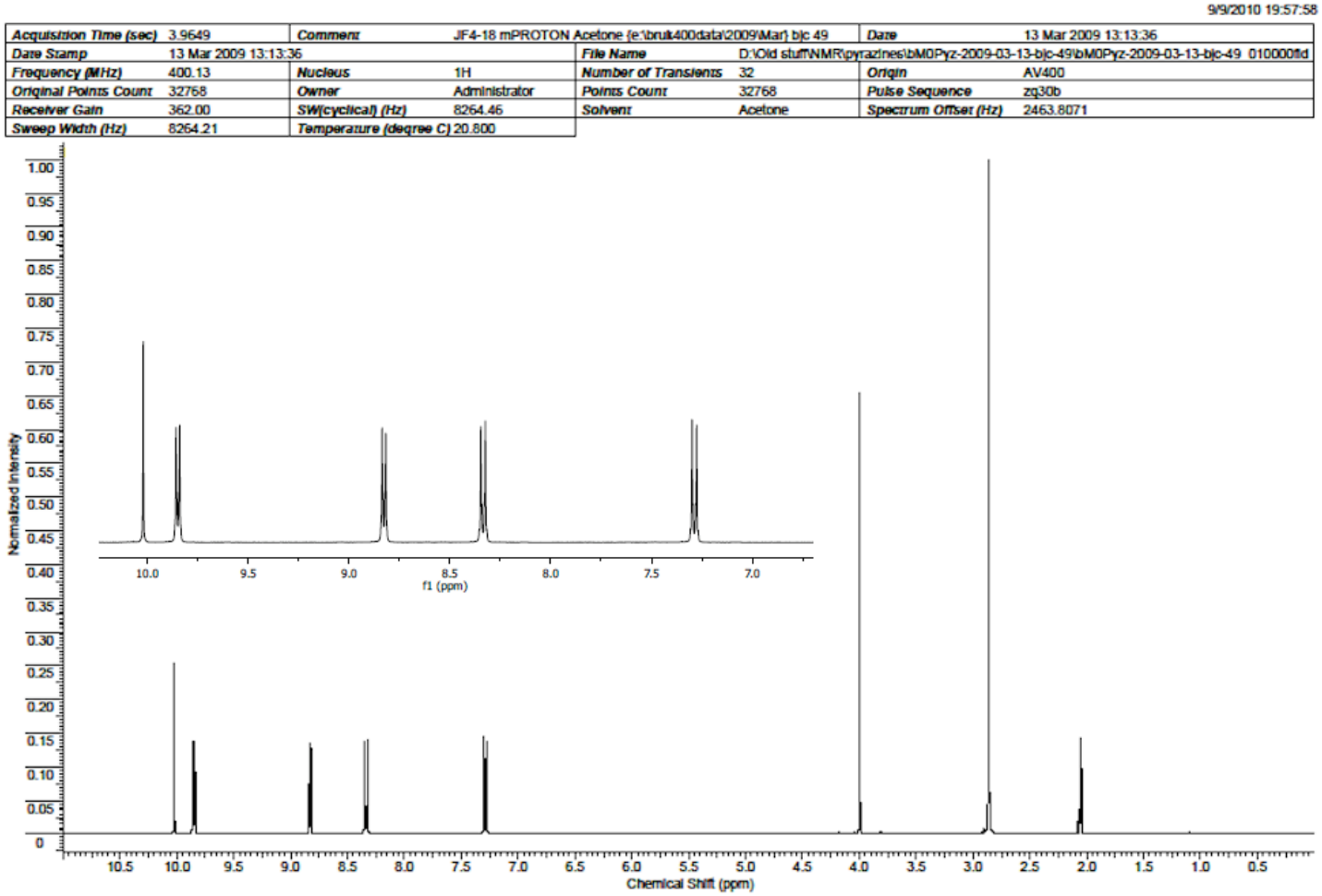

Figure S14. ^{13}C NMR spectrum of [**5**][PF_6]$_2$ (100 MHz in $(CD_3)_2SO$ at 293 K).

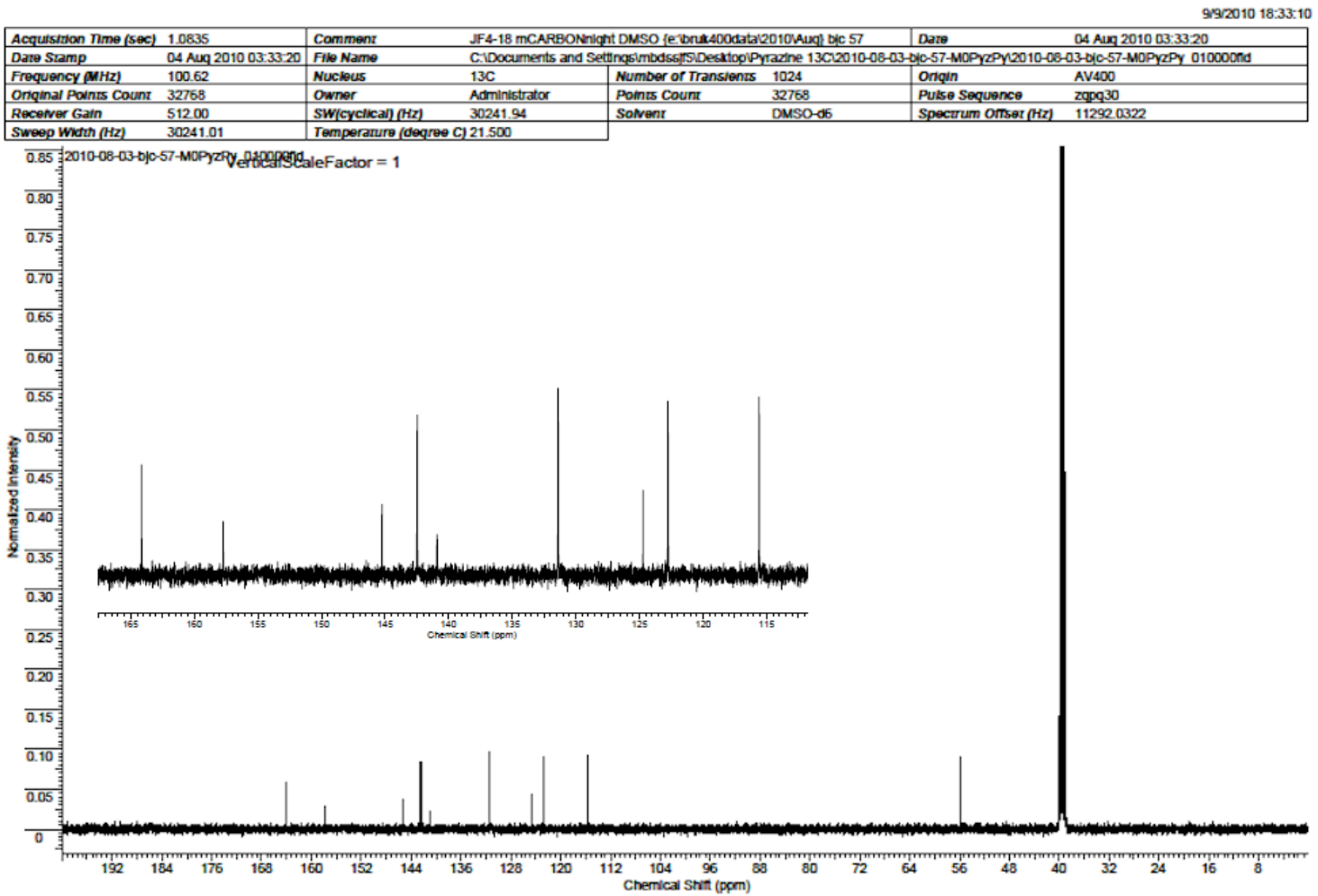

Figure S15. ^{1}H NMR spectrum of [**5**][NO_3]$_2$ (500 MHz in CD_3OD at 293 K).

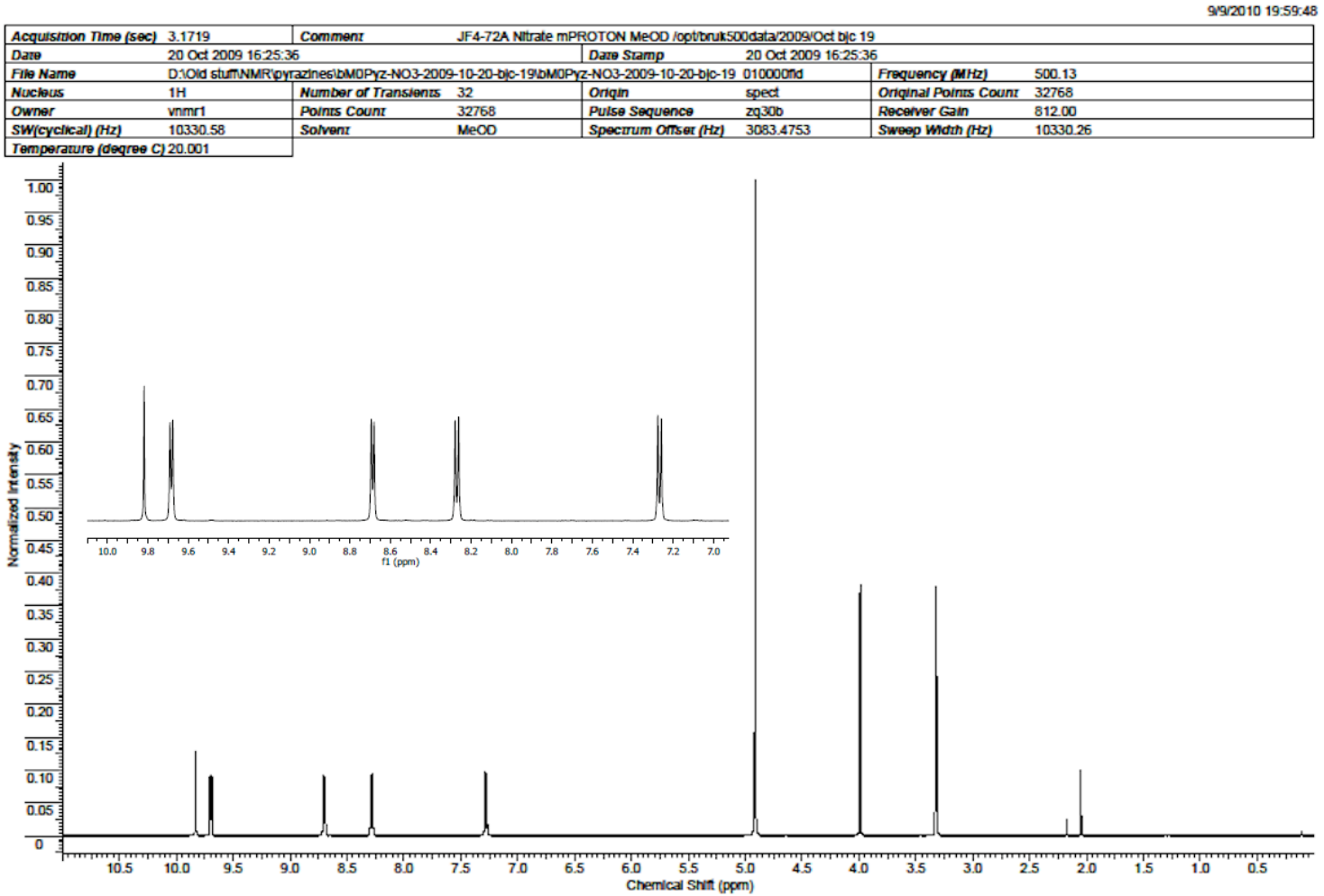

Figure S16. ^{1}H NMR spectrum of [**6**][PF_6]$_2$ (500 MHz in $(CD_3)_2CO$ at 293 K).

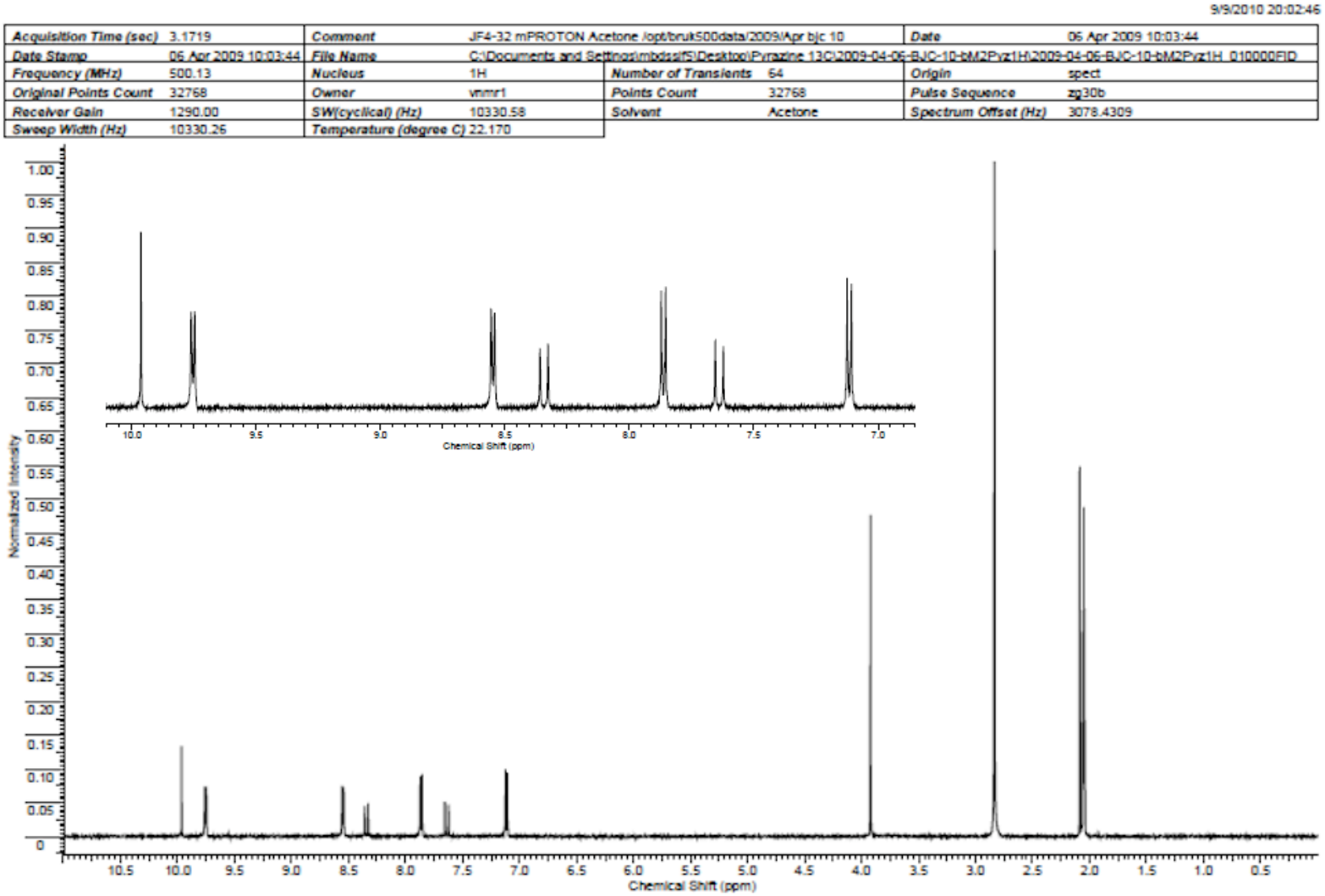

Figure S17. ^{13}C NMR spectrum of [**6**][PF_6]$_2$ (75 MHz in $(CD_3)_2SO$ at 293 K).